Reference may also here be made to Clausius' long-sustained attempt (which received some favour from Willard Gibbs in his Obituary Notice of Clausius, *Collected Papers*, ii, p. 263) to break up the Carnot cycle into two physically distinct parts, the direct transformation of heat Q′ into work at temperature θ', and a compensating transference of heat Q from temperature θ_1 to a lower temperature θ_2.]

The Absorption of the Radiation emitted by a Palladium Anticathode in Rhodium, Palladium and Silver.

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(Communicated by Prof. A. W. Porter, F.R.S. Received December 28, 1917.)

[Plate 3.]

Introduction.

The analysis of a beam of rays from an X-ray bulb by reflection at a crystal face shows that the bulb emits a continuous spectrum of radiation upon which are superposed a few wave-lengths which stand out prominently from the rest, these being the characteristic wave-lengths of the metal of the anticathode. Much note has not been taken hitherto of the general radiation, more attention having been paid to that part of the spectrum in the immediate vicinity of the characteristic rays. In the present work an attempt is made to obtain fuller knowledge of the general radiation by studying the absorption coefficients of the rays in the three elements rhodium, palladium, and silver. In the particular bulb chosen, palladium is used as the metal of the anticathode.

Apparatus.

The apparatus used in the investigation is the Bragg X-ray spectrometer, a full description of which may be found in Bragg's book on "X-ray and Crystal Structure," p. 22 *et seq.* A beam of rays, leaving the anticathode at a grazing angle, passes through two slits before falling on the crystal. The slit nearer to the crystal is movable and can be brought up very close to the crystal. After reflection, the beam passes through a third slit on its way to the ionisation chamber. We shall allude to these three slits as the bulb slit, crystal slit, and chamber slit respectively.

It is essential in an investigation of this nature to use a crystal which gives intense reflections as well as good resolution. It is not always possible to obtain these two requirements in the same crystal. Rock salt, for instance, gives fairly intense reflections, but the definition as a rule is poor; a maximum, instead of being confined to a few minutes of arc, is spread over comparatively big angles. The reason for this is that the crystal is not an accurately built one. It is made up of a number of small crystals that are slightly out of alignment, and when the crystal is rotated the reflection takes place successively at the faces of the smaller crystals. Another crystal may, on the other hand, give good definition, but the atoms of which it is composed are not such as to give intense spectra, because the intensity of the spectra depends, amongst other factors, upon the absorption coefficient of the rays in the crystal, the distribution of weight among the reflecting planes, and the thermal movement of the atoms, each of these factors depending upon the atoms composing the crystal.

The diamond is a crystal which would meet the above two requirements satisfactorily, but as a crystal of this substance was not available a search had to be made for another which would serve the purpose.

Carborundum* proved satisfactory. The reflections from the (111) face of this crystal were good both as regards definition and intensity. The structure of the crystal has not been solved, but a Laue photograph taken by passing the rays through it in a direction perpendicular to the (111) face, *i.e.*, along the hexagonal axis, points to a simple structure. The photograph is given in Plate 3.

The Spectrum of Palladium.

In order to map the spectrum of the rays emitted by the bulb, the first step is to determine accurately the position of the crystal and the ionisation chamber when a known wave-length is reflected into the chamber. The intense α-line was chosen for this purpose.

The carborundum crystal is set up on the revolving table of the spectrometer and the crystal slit brought as near as possible to it. The crystal slit is narrowed to 0·4 mm. and the chamber slit left wide open. In a rough preliminary examination the position of the ionisation chamber when the characteristic radiation is reflected into it is approximately found. The chamber is kept stationary in this position whilst the crystal is rotated,

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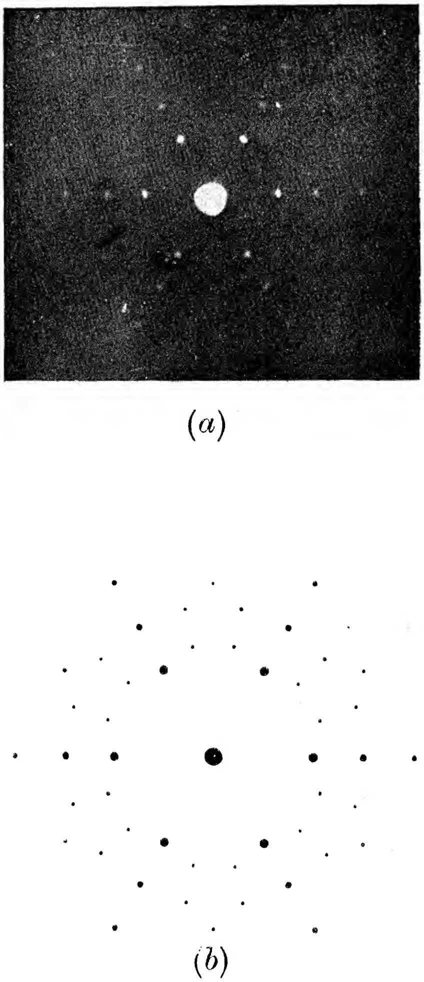
* The writer is greatly indebted to the Carborundum Company, Trafford Park, Manchester, for supplying him with excellent specimens of very nearly pure crystals of this substance. He also desires to express his sincere thanks to Mr. G. G. Blake, Richmond, in whose laboratory the Laue photograph of the crystal was taken, for supplying the necessary apparatus, and for giving liberally of his time to assist with this part of the work.



(*a*) Laue photograph of a crystal of Carborundum. Rays passed through the crystal in a direction at right angles to the (111) face.

(*b*) Diagram showing in detail the spots observed in the photograph.

observations of the ionisations produced being taken every two minutes of arc of rotation of the crystal, and every minute of arc in the immediate neighbourhood of the maximum. From these observations the exact position of the crystal when it reflects the characteristic line is determined.

The crystal is fixed in the position just found, and the chamber slit narrowed to 0·2 mm. The chamber is now rotated in the same way as the crystal was rotated previously. The sharpness of the definition of the reflected beam was very marked, and the position of the chamber when the maximum ionisation was produced could be determined very accurately, so accurately indeed that it could be used to measure the glancing angle of the rays on the crystal after applying the necessary zero correction of the spectrometer scale.

Having now fixed the positions of the crystal and the chamber for one known wave-length, the spectrum can be mapped throughout its entire range. Starting with the crystal and chamber in the positions just determined, the chamber is rotated at double the rate of the crystal, and readings taken every two minutes of arc of rotation of the crystal. The spectrum was examined in this way from a point just beyond the longest characteristic ray to the shortest ray emitted by the bulb. The form of the spectrum turned out very approximately the same from each determination, showing that the bulb was working steadily. An example of a determination is plotted in fig. 1.

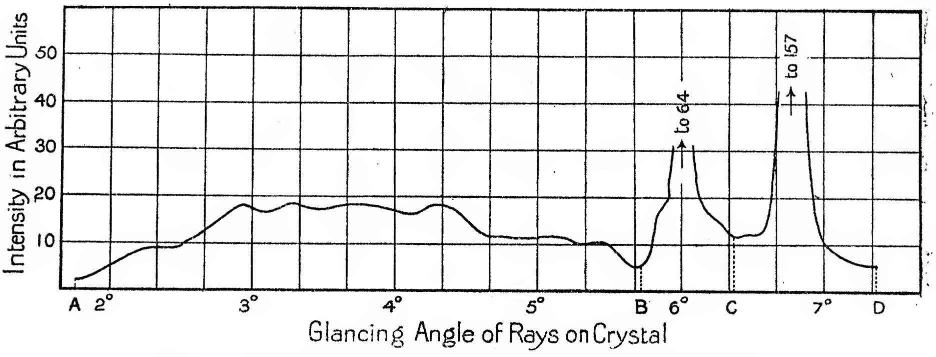


Fig. 1.—Spectrum of the rays from a palladium anticathode.

The general scattering of the rays by the crystal was inappreciable. No deflection of the leaf of the electroscope was observed during an exposure of 4 seconds—this was the exposure in each position when the spectrum was mapped—when the chamber was set at an angle different from double the glancing angle at which the rays fell upon the crystal. It was important to investigate this, in order to be certain that the effect observed when the chamber was in its correct position relative to the crystal was due to regular reflection of the rays at the crystal face, and not to a general scattering of the rays by the crystal.

Information Obtained from the Spectrum Curve.

The relation between the wave-length and the glancing angle is given by the equation $n\lambda = 2d \sin \theta$, where n is the order of the spectrum and d the distance between the reflecting planes. If λ_1 and λ_2 are two wave-lengths reflected at angles of incidence θ_1 and θ_2 respectively, then, for the same order spectrum,

$$\frac{\lambda_1}{\lambda_2} = \frac{\sin \theta_1}{\sin \theta_2}.$$

If the glancing angle corresponding to a given wave-length in the spectrum is known, then the wave-length corresponding to any other glancing angle can be calculated. The mean value of the α-line of palladium obtained by Bragg by reflection in calcite and diamond is $0{\cdot}586 \times 10^{-8}$ cm., and, in the case of carborundum, this is reflected at an angle of 6° 45′. The wave-length of the β-line of palladium, calculated from the present results, is $0{\cdot}520 \times 10^{-8}$ cm., and that of the γ-line $0{\cdot}509 \times 10^{-8}$ cm. The accuracy of the last figure is not as high as that of the β-line. These values are in close agreement with the values previously obtained by Bragg.*

The energy in the spectrum is localised in the characteristic wave-lengths of the metal of the anticathode. Integrating the spectrum curve as plotted in fig. 1, it is found that the ratio of the intensity of the wave-lengths between the points A and B to that of the wave-lengths between the points B and D is 1·12, so that, in this particular case, there is almost as much energy in the characteristic rays as in the whole of the rest of the spectrum investigated. The ratio of the intensity of the radiation between B and C and that between C and D is 1·90. This gives approximately the ratio of the intensity of the α-lines to that of the β- and γ-lines. This integration was also carried out experimentally by rotating the crystal at a definite rate through each of the maxima, and noting the total amount of ionisation produced in each case. The mean value obtained for the ratio by this method was 1·93, which agrees very closely with the value just obtained by the direct integration of the spectrum curve.

The spectrum shows a minimum of intensity at the glancing angle 5° 41′, corresponding to a wave-length $0{\cdot}493 \times 10^{-8}$ cm. This suggests selective absorption of this wave-length by the crystal, which would be the case if the characteristic radiation of the J series of one of the atoms composing the crystal were excited. From observations on other crystals, and in view of the results that are to follow, we would assign this wave-length, namely, $0{\cdot}493 \times 10^{-8}$ cm., to the β-line of the J series of silicon, assuming that the J-radiations are of constitution similar to the K-radiations. The β-lines of the J-radiations of oxygen and carbon, calculated on the basis of the relative values of the wave-lengths of aluminium, oxygen, and carbon, as experimentally determined by Barkla and White,* work out to be about $0{\cdot}519 \times 10^{-8}$ cm. and $0{\cdot}559 \times 10^{-8}$ cm. respectively. These figures are in fair agreement with those deduced by Barkla by the ionisation method, but are somewhat higher than the values obtained by him by the absorption method.

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* W. H. Bragg, 'Phil. Mag.,' vol. 29, March, 1915.

Another feature of the spectrum is the rather prominent maximum at about 4° 20′, corresponding to a wave-length of about $0{\cdot}38 \times 10^{-8}$ cm. It is hoped later to investigate this region of the spectrum more in detail than has been done up to the present.

The shortest wave-length emitted by the bulb under the conditions of working in the experiment was about $0{\cdot}15 \times 10^{-8}$ cm. The spectrum shows that, from this wave-length to that of the longest characteristic wave-length of the anticathode, there exists a continuous band of wave-lengths, and in this particular case the relative intensities remained approximately constant.

It is, of course, to be expected that the distribution of energy in the spectrum would vary greatly, according to the state of the bulb, and it would be of interest to find what effect the alteration of voltage and current would have on the form of the spectrum curve.

The Intensities of the Different Order Spectra of the Characteristic Lines of Palladium in Carborundum.

It will be necessary to know how the intensities of the spectra decline as we proceed to higher orders, in order to account for some apparent irregularities observed in the absorption of rays from different parts of the spectrum. These were measured in the case of the two peaks, giving the α_1, α_2 and β, γ lines respectively, and in each case the rate of decline was the same. Different widths of slits were used, but it was found that this had but a slight effect upon the intensities. The relative intensities of the orders were as follows:—

100·0, 37·9, 18·0, 10·6, 2·8, 0·6.

These are plotted in fig. 2, and it will be seen that they fall along a smooth curve, except for the fourth order, which is too large. The planes parallel to the (111) face of carborundum are therefore not all similar, such as, for example, the (100) planes of rock salt, and the rate of fall of intensity differs from that of the normal fall of intensity as generally assumed.

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* Barkla and White, 'Phil. Mag.,' vol. 34, October, 1917.

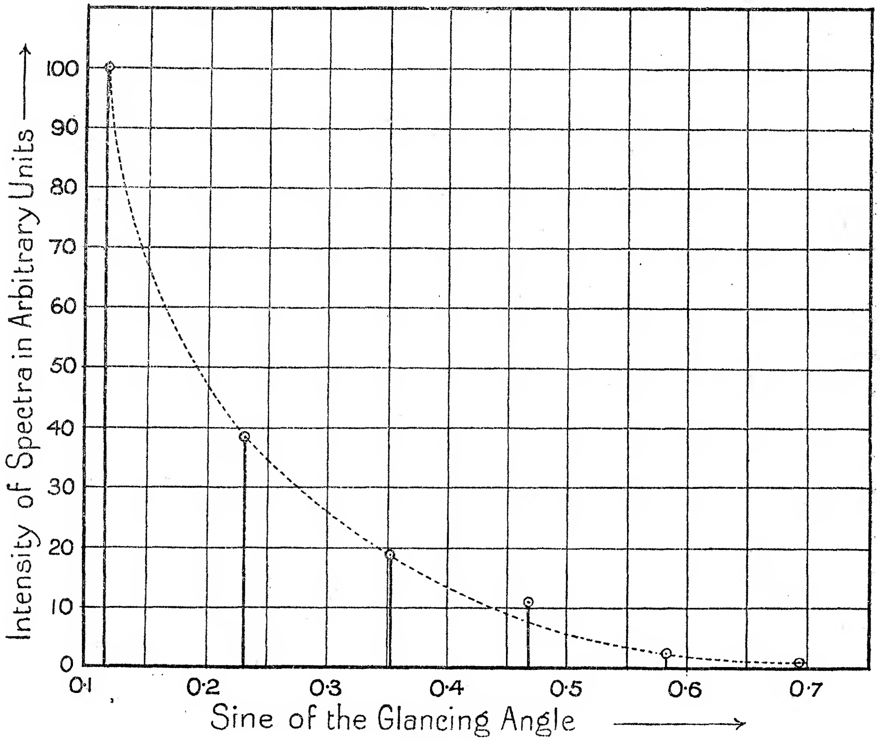

Fig. 2.

We shall assume in the calculation that follows that the different order spectra of all the wave-lengths in the spectrum follow the same rate of decline as do those of the α and β peaks.

Measurements of Absorption Coefficients.

The absorption of the rays in the spectrum was measured in the three metals rhodium, palladium, and silver. For this part of the work the width of the chamber slit was 1 mm., the bulb and crystal slits remaining the same as previously, namely, 2·0 mm. and 0·4 mm. respectively. No appreciable difference was observed in the amount of ionisation produced in the chamber for a given exposure when the absorbing screen was placed near the crystal and when it was placed near the chamber slit. It was finally fixed at about 2 cm. in front of the chamber slit. The ionisations produced in the chamber, with and without the screen in front of it, were measured, and the value of the absorption coefficient determined by means of the equation $I = I_0 e^{-\mu x}$, where I_0 is the initial intensity, and I the final intensity after traversing a screen of thickness x cm. The accuracy of the method of measurement employed depends upon the constancy of the bulb, but, by measuring the ionisation without the screen before and after that with the screen, and multiplying observations, fairly accurate mean values were obtained for the absorption coefficients.

The present investigation is to be regarded as a preliminary one, and it is hoped with the new apparatus now under construction to employ a method which will be independent of the output of the bulb both as regards wave-length and intensity.

The values of the absorption coefficients here determined refer to the total absorption of the radiation in the absorbing screen. This absorption is made up of the scattering absorption and the fluorescent absorption, the latter being itself constituted of the absorption of the various fluorescent X-radiations, J, K, L, ..., excited in the absorbing screen, together with the corpuscular radiations which accompany each of these fluorescent radiations. We have then $\mu/\rho = \sigma/\rho + \tau/\rho$, where μ/ρ is the total absorption coefficient, σ/ρ the scattering coefficient, and τ/ρ the fluorescent coefficient. Barkla finds that the scattering of X-rays of very short wave-length by equal masses of various substances varies only little with the atomic weight of the scattering element. There is a slight increase of the mass scattering coefficient with an increase in the atomic weight of the scatterer, but this increase is more marked with X-radiation of greater wave-length, until for long waves it is very considerable. As we are dealing here with short waves we may assume without introducing serious error that the mass scattering coefficient is constant for the absorbing substances we are using, and also that it is independent of the wave-length over the range of wave-lengths that we are investigating. The value found by Barkla for σ/ρ, when the wave-length of the radiation is short, is 0·2. This is small compared with the values of the total absorption coefficient μ/ρ found for the elements rhodium, palladium, and silver, with the wave-lengths here employed. It does not exceed 4 per cent. of the smallest value of μ/ρ determined, so that its effect is almost within the limits of experimental error. We shall, however, apply this correction for the scattering to bring the results into line with those already published by Barkla and White* for the light elements, in whose case the scattering plays a prominent part.

In fig. 3, the logarithm of $(\mu/\rho - 0{\cdot}2)$, *i.e.*, the logarithm of τ/ρ, is plotted against the logarithm of the corresponding wave-length in the case when the absorbing screen is rhodium. The curves obtained with palladium and silver are similar to that of rhodium. The three curves are very near together, and in order to avoid confusion only the rhodium curve is included in the diagram.

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* Barkla and White, *loc. cit.*

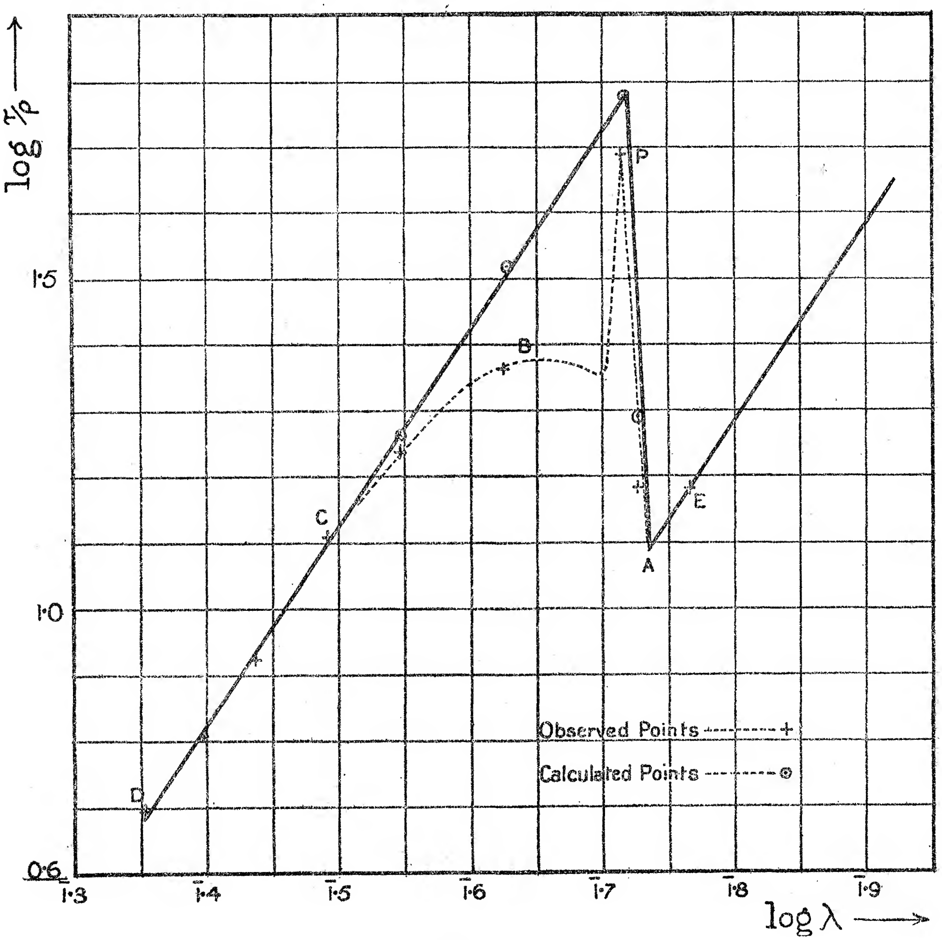

Fig. 3.

The graph shows that the absorption of the rays is normal until we reach the point A, where, as we proceed to shorter wave-lengths, the absorption coefficient increases rapidly and follows approximately the curve ABC, except for a singular point P, which is very far removed from this curve. The reason for this apparent irregularity will shortly be explained. Beyond the point C the absorption curve follows approximately a straight line course. The radiations corresponding to this latter part of the curve constitute the "end radiations" of the bulb.

To explain the existence of the curved portion ABC of the absorption curve, we have to refer to the spectrum of the rays from the bulb mapped out in fig. 1. It will be seen that the radiations reflected at angles greater than 4° have superposed upon them radiations of shorter wave-length which constitute the second order spectra of the shortest waves emitted by the bulb. It is therefore to be expected that the mean wave-lengths of the rays corresponding to the curved portion of the absorption curve will be shorter than those calculated from the angle of incidence on the assumption that the rays are all of the first order spectrum. Consequently the absorption coefficient of the rays in the absorbing screen will be too small. The effect of the superposed second order spectra will be considerable for radiations reflected from the crystal face at angles in the neighbourhood of 5°, because the intensity of the second order spectra forms a fairly high percentage of the total intensity of the radiation in this portion of the spectrum. On the other hand, the effect of the superposition of the second order spectra on the wave-lengths of the characteristic lines will be small, because the intensity of these lines is so great compared with that of the radiations superposed upon them. This is the reason why the point P in the absorption curve, which represents the absorption of the intense β-line, is so far removed from the curve ABC. It will be seen from the curve that the correction applied to the observed value of the absorption coefficient of the β-waves to obtain the correct value is quite appreciable. In the case of the α-wave, however, which is represented by the point E, the correction is negligible.

The exact shape of the observed absorption curve depends upon the form of the spectrum emitted by the bulb, and it should be pointed out that the dotted portion ABC represents only very roughly the conditions obtaining in the particular case in question.

The above considerations show that the homogeneity, or, in other words, the purity, of the characteristic lines emitted by a bulb and isolated by reflection at a crystal face will depend, to a certain extent, upon the state of working of the bulb.

Calculation of the True Absorption Coefficient of each Wave-length in the Spectrum.

Assuming that the longer wave-lengths in the spectrum are modified by the superposed wave-lengths of the second order spectra of the shorter wave-lengths, we can easily calculate the true absorption coefficient of each wave-length in the spectrum.

Let ${}_2I_0$ be the intensity of the shorter wave superposed upon the longer wave whose intensity is ${}_1I_0$, so that the total intensity is $({}_1I_0+{}_2I_0)$. If I_1 be the intensity of the longer wave after transmission through an absorbing screen of thickness x cm., we have

$$I_1 = {}_1I_0 e^{-\mu_1 x},$$

where μ_1 is the true total absorption coefficient of the longer wave in the screen.

Similarly for the shorter wave-length

$$I_2 = {}_2I_0 e^{-\mu_2 x},$$

where μ_2 is the true total absorption coefficient of the shorter wave in the screen.

The value of the total absorption coefficient μ, as measured in the present work, is given by the relation

$$I_1 + I_2 = ({}_1I_0 + {}_2I_0)\, e^{-\mu x},$$

i.e.

$${}_1I_0 e^{-\mu_1 x} + {}_2I_0 e^{-\mu_2 x} = ({}_1I_0 + {}_2I_0)\, e^{-\mu x},$$

so that

$$e^{-\mu_1 x} = \frac{({}_1I_0 + {}_2I_0)\, e^{-\mu x} - {}_2I_0 e^{-\mu_2 x}}{{}_1I_0}, \qquad (1)$$

which gives the value of μ_1, the true total absorption coefficient of the longer wave without the superposition of the shorter component.

In the present case it suffices to consider only the superposition of the second order spectra, since we are only investigating that portion of the spectrum from the shortest wave-lengths to those of the characteristic lines. This forms but a small part of the whole spectrum, and for longer waves we would have to consider the superposition of spectra of higher order than the second. The expression for the true total absorption coefficient in the general case when several spectra are superposed upon the wave-length considered would be

$$e^{-\mu_1 x} = \frac{e^{-\mu x}\Sigma_1 I_0 - ({}_2I_0 e^{-\mu_2 x} + {}_3I_0 e^{-\mu_3 x} \ldots)}{{}_1I_0}. \qquad (2)$$

This expression holds for any wave-length in the spectrum. To evaluate the expression on the right-hand side of equation (1), we require to know the intensity of the shorter wave-length, that of the longer wave-length, and the true total absorption coefficient μ_2 of the shorter wave-length; μ is known, being the quantity measured in the experiment.

An examination of the end radiations of the bulb showed that the rays reflected at definite angles in this part of the spectrum were homogeneous as far as could be determined by absorption in sheets of silver. The short waves superposed upon the longer waves in the region ABC of the absorption curve will be the second order spectra of these homogeneous radiations, and since the rate of decline of intensities of the various order spectra is known from fig. 2, which is assumed to be the same for each wave-length in the spectrum, the initial intensity ${}_2I_0$ of the shorter wave can be calculated. Also the true total absorption coefficient μ_2 of this radiation is directly determined in the experiment.

The form of the spectrum mapped out on different occasions showed the same characteristics, and the relative intensities of the different wave-lengths remained approximately constant. The intensity ${}_1I_0$ of the longer wave-length may therefore be obtained by subtracting the calculated intensity of the shorter wave-length from the observed total intensity.

We have therefore the data required to calculate the value of the true total absorption of the pure radiation corresponding to any part of the spectrum. Carrying out this calculation for the points observed in the region ABC, the calculated points fall very approximately along the continuation of the straight line DC up to the wave-length corresponding to the point P. Afterwards there is a rapid fall, until that point is reached at which the characteristic radiation is excited, when the absorption coefficient begins to increase again with increase of wave-length of the exciting radiation.

Table I gives the true fluorescent coefficient τ/ρ in rhodium, palladium, and silver for a number of wave-lengths. The figures give the observed values corrected for scattering and for the general radiation emitted by the bulb.

Table I.

Absorber.					
Rhodium.		Palladium.		Silver.	
$\lambda \times 10^8$.	τ/ρ.	$\lambda \times 10^8$.	τ/ρ.	$\lambda \times 10^8$.	τ/ρ.
0·226	4·92	0·226	5·13	0·226	5·53
0 249	6·44	0·268	8·61	0·268	9·29
0·273	8·51	0·312	13·8	0·312	14·5
0·312	12·9	0·363	21·5	0·363	22·8
0·353	18·4	0·396	27·4	0·396	29·6
0·424	32·5	0·465	45·0	0·465	47·8
0·520	58·2	0·511	14·8	0·499	15·9
0·537	19·3	0·520	11·2	0·520	12·15
0·586	15·1	0·586	15·9	0·586	17·3

The slope of the straight line DC gives the index three very approximately, so that the relation between wave-length and the absorption coefficient becomes

$$\tau/\rho = K\lambda^3$$

where the value of K varies for different substances, but is a constant for a given substance over the range of wave-lengths between the absorption bands of that substance. This confirms the relation already obtained by Hull and Rice* for the absorption of the end-radiations of a Coolidge tube in aluminium, copper, and lead, and that obtained by Barkla and White† in the case of the light elements.

The Wave-length Necessary to Excite the Characteristic Radiation of a Substance.

The point at which the characteristic radiation of the absorber is excited is very definitely marked. The absorption curves show that the characteristic radiation of the absorber is not excited by a radiation of a wave-length equal to that of the longest characteristic wave of the substance. It requires a shorter wave-length to do this. When the wave-length which excites the characteristic radiation is reached, both the α- and the β-lines are emitted together; it does not seem possible to excite the α-radiation without exciting the β-radiation. The approximate values deduced from the absorption curves for the wave-length necessary to excite the characteristic radiations of rhodium, palladium, and silver are given in Table II.

Table II.

Absorber.	Longest wave-length necessary to excite the characteristic rays.
Rh	0·545 × 10^{-8} cm.
Pd	0·508
Ag	0·495

In each case the critical wave-length lies in the neighbourhood of the β-line of the spectrum, which points to the β-line as being the critical wave-length necessary to excite the characteristic radiation of a substance.

Ledoux-Lebard and Dauvillier,‡ investigating this point by another method, have arrived at the same conclusion. They examined the K-radiations of tungsten, which consist of four lines similar to those in the K series of palladium. Applying different voltages to the tube, they found that a voltage sufficiently high to excite the β-ray had to be reached before the α-characteristic lines were emitted.

Bragg§ suggests that the characteristic rays of a substance might form a system which can only be excited as a whole. To decide whether it is necessary to excite the γ-ray before the other rays are excited, more observations will have to be taken of the absorption coefficients in the neighbourhood of the critical point. This is at present in progress.

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* Hull and Rice, 'Phys. Rev.,' vol. 8, 1916, p. 326.

† Barkla and White, *loc. cit.*

‡ Ledoux-Lebard and Dauvillier, 'Comptes Rendus,' December, 1916.

§ W. H. Bragg, 'Phil. Mag.,' vol. 39, March, 1915.

Summary.

(1) A short account is given of some preliminary experiments carried out with the rays from an ordinary X-ray bulb.

(2) A spectrum of the rays from a palladium anticathode is obtained over a limited range of wave-lengths by reflection in the (111) face of a carborundum crystal. The spectrum shows that the bulb emits a continuous band of wave-lengths upon which are superposed the characteristic rays of the metal of the anticathode, and, under the conditions of working in this particular case, the relative intensities of the different wave-lengths in the spectrum remained approximately constant.

(3) There is a minimum of intensity in the spectrum corresponding to the wave-length $0{\cdot}493 \times 10^{-8}$ cm. On the assumption that the minimum is due to the selective absorption of this wave in the crystal, the value $0{\cdot}493 \times 10^{-8}$ cm. is assigned to the β-line of the J-series of silicon. From the experimental results of Barkla and White on the J-series of the elements Al, C, and O, the approximate values deduced for the β-line of the J-series of oxygen and carbon are $0{\cdot}519 \times 10^{-8}$ cm. and $0{\cdot}559 \times 10^{-8}$ cm. respectively.

(4) Assuming Bragg's mean value of the α-line of palladium to be $0{\cdot}586 \times 10^{-8}$ cm. the following values are obtained for the wave-lengths of the β- and γ-lines:

$$\beta = 0{\cdot}520 \times 10^{-8}, \qquad \gamma = 0{\cdot}509 \times 10^{-8} \text{ cm.}$$

(5) The absorption coefficients of the rays from the bulb have been measured in rhodium, palladium, and silver. The results show that the relation between wave-length and absorption coefficient is expressed by the relation

$$\tau/\rho = \mathrm{K}\lambda^3$$

where τ/ρ is the fluorescent coefficient and K is a constant for a given substance over the range of wave-lengths between the absorption bands of that substance.

(6) The critical wave-length necessary to excite the characteristic rays of a substance lies in the neighbourhood of the β-ray of that substance. The α-ray is not excited until the β-ray is excited.

(7) It is pointed out that the purity of the characteristic lines emitted by

a bulb and isolated by reflection at a crystal face will depend to a certain extent upon the state of working of the bulb.

In conclusion, I wish to express my indebtedness to Prof. W. H. Bragg, F.R.S., for his kindness in putting his spectrometer at my disposal, without which the work could not have been undertaken. Also, my best thanks are due to Prof. A. W. Porter, F.R.S., for the valuable help he has given me throughout the course of the work.

Selenic Acid and Iron.—Reduction of Selenic Acid by Nascent Hydrogen and Hydrogen Sulphide.—Preparation of Ferrous Selenate and Double Selenates of Iron Group.

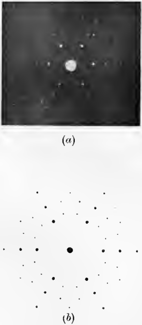
By A. E. H. Tutton, D.Sc., M.A., F.R.S.

(Received February 7, 1918.)

Exceptional difficulties have been met with in the preparation of the iron (ferrous) group of double selenates of the monoclinic isomorphous series $R_2M\left(\begin{matrix}S\\Se\end{matrix}O_4\right)_2, 6H_2O$, and some new and unexpected chemical facts have been revealed, which form the subject of this communication. When the author, in pursuing the course of the crystallographic and physical investigation of the double selenates of this grand series on exactly parallel lines to those followed in the completed investigation of the corresponding double sulphates, arrived at the iron group, three difficulties were encountered. The first was that of preparing the simple salt ferrous selenate, common to the group. The second was the rapid decomposition, with brown deposition, of the aqueous solution of any ferrous selenate obtained, also that of the mixed solution obtained by adding to the latter solution a solution of the molecular equivalent of the alkali selenate, with the object of preparing any one of the four salts of the group,

$$K_2Fe(SeO_4)_2,6H_2O,$$
$$Rb_2Fe(SeO_4)_2,6H_2O,$$
$$Cs_2Fe(SeO_4)_2,6H_2O,$$
$$(NH_4)_2Fe(SeO_4)_2,6H_2O.$$

The third difficulty was offered by the fact that no crystals of the potassium ferrous salt were ever obtained at all.



(a) Laue photograph of a crystal of Carborundum. Rays passed through the crystal in a direction at right angles to the (111) face.

(b) Diagram showing in detail the spots observed in the photograph.